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Nutrient budgets and river impoundments: Interannual variation and implications for detecting future changes

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Abstract

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Temporal variability at monthly and annual scales was quantified at the inlets and outlets of 3 sequential impoundments for total phosphorus, dissolved phosphorus (TP), total nitrogen (TN), dissolved nitrogen, particulate nitrogen, colored dissolved organic matter, specific conductance, and pH over three years. Chlorophyll *a* (Chl-*a*) was measured within the largest of the 3 impoundments; Secchi disk transparency depth was measured over 9 years. The data were analyzed to characterize "ordinary" temporal variability, and statistical models were constructed to evaluate the sampling effort that would be required to detect predicted changes in response to a municipal ordinance banning phosphorus in lawn fertilizers, as well as to possible removal of the dam forming the middle impoundment. Changes of 25% in monthly mean value would require weekly samples during the summer for only 1 or 2 years for TN and TP, but about 8 years for Chl-*a* to achieve statistical confidence that conditions had changed. Bioassay experiments in the most upstream and largest of the 3 impoundments indicated that water residence times are in general too short to permit phytoplankton the opportunity to develop populations large enough to alter biogeochemistry substantially in any of the impoundments. Mass balance calculations tended to confirm this conclusion; the reservoirs acted neither as nutrient sources nor sinks over the period of study.

Key words: alkaline phosphatase, nutrient bioassay, nutrient budgets, sampling requirements, silica, temporal variation, watershed

Detecting the effects of anthropogenic activities on aquatic ecosystems and discriminating them from natural interannual variation is a persistent challenge to environmental studies. Water monitoring programs by state and municipal governments are often predicated on the idea that they provide a useful reference against which unusual perturbations can be identified. But the practical definition of "unusual" perturbation is tempered by "ordinary" temporal variability, which imposes limitations on the magnitudes of changes that can be detected with statistical confidence.

In a recent communication, Knowlton and Jones (2006) considered the important question of sampling effort necessary to detect changes in trophic state indicators for impoundments within Missouri, USA. Based on their model of variance, they concluded that 3–8 years of monthly samples might be needed to detect 2-fold step changes in a typical seasonal mean with statistical confidence, and that more than a decade might be needed to detect an increasing linear trend for variables that are doubling every 20 years. If the patterns of "ordinary" temporal variation they found are typical, then routine monitoring efforts might require long-term, even generational, commitment to yield meaningful information when conditions are changing by less than a factor of 2 every 2 decades.

The Huron River of southeastern Michigan, USA, like many other rivers transecting the heartland of America, inherits a legacy of rural agriculture, patchwork urbanization, and fragmented management efforts. The main stream was heavily modified during the early 20th century to generate hydroelectric power. Detroit Edison developed most of the river valley, starting in 1912 at Barton Dam, which formed Barton Pond and became the main drinking water supply for the city of Ann Arbor. This study focuses on Barton Pond and 2 successive downstream impoundments, Argo Pond and Geddes Pond. Together, these impoundments represent

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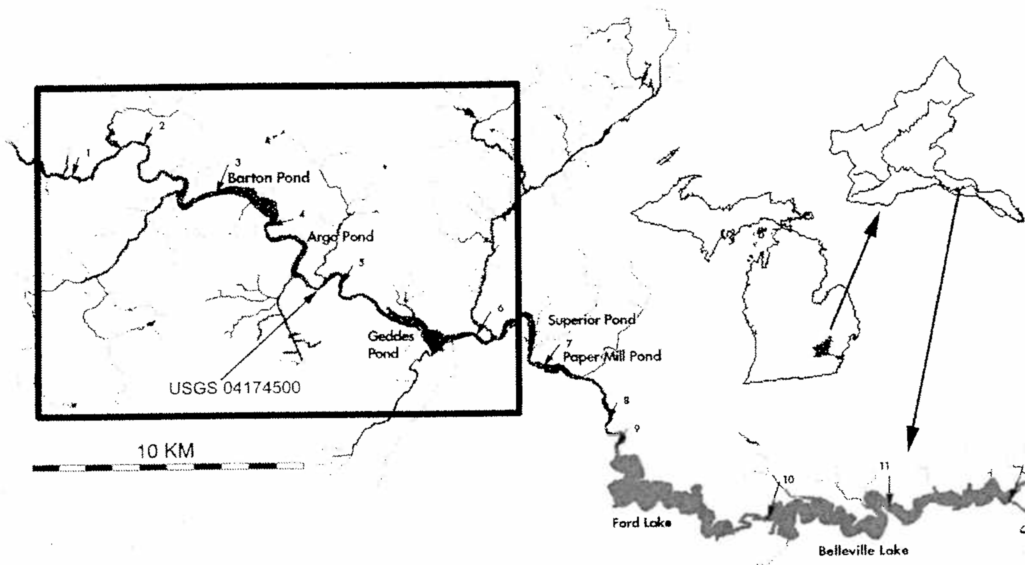

Figure 1.-Study site enclosed by rectangle. Sampling locations are indicated by arrows and numbers.

a reservoir chain with connecting river segments that provide not only drinking water and hydroelectric power, but also intensive recreation. On-going and proposed development activities could alter future nutrient income and trophic condition by permitting discharge of treated wastewater into the river above Barton Pond. There is also a proposal under study to remove Argo Dam and drain much of the pond, restoring the historical river course and opening new river frontage and land.

Prompted by environmental concerns, Ann Arbor enacted an ordinance in 2006 that restricted the use of phosphorus-containing fertilizers based on expectations that full compliance could reduce phosphorus loading to the Huron River by 22% (M. Naud, pers. comm. 7 Dec 2007; Anon. 2006).

These activities, or others like them being considered throughout the watershed, could provoke ecosystem-level changes. A fair question would be how much perturbation in water quality, and how much sampling effort, would be needed for changes to be recognized. To evaluate future changes in state variables, it is essential to establish a frame of reference that incorporates the variability scales associated with the reference conditions. Even if perturbations are far from subtle, "ordinary" interannual variation may mask the effects despite several years of observation. The purpose of this study was to document initial conditions of 3 impoundments over 3 to 9 summer seasons (Jun–Sept), and to deduce the sampling effort required to decipher future changes. Environmental variables deemed of particular interest included dissolved and particulate phosphorus (P), dissolved and particulate nitrogen (N), dissolved organic carbon (DOC), and soluble reactive silica (SRSi). We also tried to determine whether phytoplankton dynamics within the impoundments were significant to their roles as nutrients sources or sinks and, thus, the degree to which the impoundments functioned as self-contained biogeochemical systems as opposed to wide places in the river where the chief significance was variable but short retention time (Pridmore and McBride 1984, Søballe and Kimmel 1987).

Materials and methods

Study site

Our field site was the middle portion of the Huron River catchment in southeastern Michigan (United States Geological Survey, USGS Cataloging Unit 04090005; Fig. 1). Barton Pond (42.31°N, 83.75°W) has a surface area of 788,000 m^2 and volume of 2,285,000 m^3, based on bathymetric maps provided by Ann Arbor. The volumes of Argo and Geddes ponds are reported to be 669,000 m^3 and 1,532,000 m^3, respectively (Quets 1991). All of the impoundments are operated as run-of-the-river, meaning that stage heights are held nearly invariant through automated hydraulic operation of discharge gates.

Field sampling

Water was collected from the inlets and outlets of Barton, Argo, and Geddes ponds from June 2003 to September 2005. Sampling was at weekly intervals or more frequently from April to November, and biweekly from December to March.

Table 1.-Bioassay experiments conducted from February to May 2005 using Barton Pond. Alkaline phosphatase (AP) was not measured in experiment B3.

Experiment	Duration	Procedure and Treatment
B1	18–24 Feb 05	Four controls; four replicate additions of ca. 0.3 μM P.
B2	18–24 Mar 05	(Identical to B1)
B3	15–21 Apr 05	Four controls; four replicate additions of ca. 50 μM Si.
B4	22–28 Apr 05	(Identical to B3)

Vertical profiles of temperature and dissolved oxygen, Secchi transparency depth, and raw water for nutrient analysis were obtained from Barton Pond near the outlet dam by personnel from the City of Ann Arbor Water Utilities during most of the ice-free season (T. Hejke, pers. comm.). Surface grab samples were obtained at the dam during ice cover. Raw water was filtered on site for nutrient analysis using Millipore™ disposable filter capsules of nominal 0.45 μm pore size.

Nutrient analyses

Nutrient analyses included SRSi, particulate silica (Part-Si), soluble reactive phosphorus (SRP), dissolved phosphorus (DP), total phosphorus (TP), dissolved nitrogen (DN), particulate nitrogen (PN), ammonium (NH_4) and nitrate (NO_3). Additionally, samples from Barton Pond were processed for alkaline phosphatase (AP), chlorophyll (Chl-*a*, Chl-*b*, Chl-*c*), and phycocyanin (PC) concentrations. Specific conductance at 25 °C (K_{25}) was measured with samples at 25 °C in a water bath. Colored dissolved organic matter (CDOM) was measured as UV absorbance at 254 nm. Dissolved organic carbon (DOC) was measured by Shimadzu TOC analyzer. Dissolved organic N (DON) was calculated as the difference between DN and the sum of ammonium and nitrate. All nutrient analyses were performed according to Ferris and Lehman (2007).

Bioassay Experiments

Bioassay experiments were conducted with water from Barton Pond to examine algal growth potential as well as potential limiting nutrients, with particular attention to diatoms. Four experiments were conducted from February to May 2005. Experimental setups and nutrient analyses were performed according to Ferris and Lehman (2007), at 22 °C under continuous illumination for 6 days; the treatments involved additions of P as phosphate or Si as silicate to raw water samples (Table 1).

Nutrient fluxes

Fluxes of DP, TP, NO_3, DN, and TN were calculated for Barton, Argo, and Geddes ponds and were used to determine nutrient balance. Daily concentrations at inlets and outlets were linearly interpolated from measured concentrations, after we had established that there were no strong correlations between concentrations and river discharge (see results).

Daily discharge records for the Huron River at Ann Arbor were obtained from USGS on-line archives for station 04174500. This gaging station is located between Argo and Geddes ponds. Daily water income to Argo Pond was adjusted by applying a factor of 0.985 to the USGS data, based on the logic that the catchment area is 1.5% smaller at the inlet of Argo Pond than at the gaging site itself. Daily water discharge from Geddes Pond was adjusted by a factor of 1.034 to represent the incremental catchment area at that point downstream. Daily volumes of drinking water withdrawn from Barton Pond were obtained from the city of Ann Arbor. River discharge into Barton Pond was adjusted to account for this diversion as well as for the catchment area correction factor of 0.946. Water discharging from Barton Pond was calculated as the sum of water passing the Barton dam to flow into Argo Pond plus the water pumped out of the Pond for municipal water supply. The water intakes are situated within the Pond, in close proximity to the dam.

Nominal flushing times (T_f) were calculated using outflow Q (m^3/d) and pond volumes, V (m^3). For any given arbitrary starting day, designated t = 0, T_f was calculated from the implicit function:

$$V = \int_0^{T_f} Q\, dt \qquad (1)$$

Statistical distributions of river discharge (Q) and water chemistry variables were inspected, and transformed to approximate Gaussian by natural logarithm as appropriate. Statistical methods, typically one-way and two-way analyses of variance (AOV) and linear regression were conducted using Microsoft Excel™ and SYSTAT 10 to test for effects of year, month, or year-month interactions. When strong temporal effects were present, the following algorithm was adopted for detecting whether future conditions exceed "ordinary" variability:

1. Define the mean (X_i) and sample variance (s^2) associated with each year-month combination.

2. Average k separate distributions (where k is number of different years, *e.g.*, May of 2003, 2004, and 2005) with equal weight such that

$$Var(Xmean) = 1/k \times \sum_{i=1}^{k} Var(X_i) \qquad (2)$$

3. For each distribution thus estimated, the mean is assumed equal to the sample mean, however, the sample variance is itself an estimate. For significance testing, therefore, the variance of each distribution (*i.e.*, $Var(X_i)$) was estimated as the 90% upper confidence limit of the sample variance, defined as

$$(n-1)s^2 / \chi^2_{0.9;n-1} \qquad (3)$$

where s^2 is sample variance (Eq. 2) with n-1 degrees of freedom.

4. Perform a power calculation to ascertain the sample size, n, necessary to detect hypothetical differences in monthly mean value from those of putative 'ordinary' values at $\alpha = 0.1$ and $\beta = 0.75$.

The rationale for this approach is that the variance of the multi-year distribution defined in Eq. 2 is well constrained, and possibly overestimated, by the confidence level established through Eq. 3. The object was to hold Type I error reasonably low, while seeking a credible level of power to detect environmental changes if they indeed occur. We estimated power and requisite sample size n using standard normal cumulative distributions $Z\alpha$ and $Z\beta$ where

$$n = [\sigma(Z\alpha - Z\beta)/\Delta X]^2 \qquad (4)$$

and ΔX is the magnitude of the change, σ is the standard deviation of the distribution estimated in Eq. 2, and n is required sample size. The critical values of $Z\alpha$ and $Z\beta$ under these conditions are 1.64 and −0.68, respectively.

Results

Bioassay

Bioassay experiments demonstrated diatom growth potential in the laboratory. Part-Si increased for all experimental treatments, including Control, ranging from 2.4 to 12.6-fold with respect to initial conditions. In some experiments, final silica concentrations dropped as low as 0.7 μM. Experiments with P additions show an increase in chlorophyll and PN (Table 2), but no significant increase in Part-Si, indicating no enhanced diatom growth over Control. For Si additions, there was no enhanced growth with respect to Control.

Table 2.-Statistical significance of nutrient additions. Experiments were subjected to one-tailed t-tests. All contrasts are with respect to Control. NS = not statistically significant. There were no statistically significant responses measured for either Chl-*c* or Part-Si.

	Treatment	Chl-*a*	Chl-*b*	PN
B1	+P	<0.001	0.001	<0.001
B2	+P	NS	0.005	0.002
B3	+Si	NS	NS	NS
B4	+Si	NS	NS	NS

Table 3.-Initial final alkaline phosphatase (AP) activity in bioassay experiments. Units are nmol 4-methylumbelliferyl phosphate (MUP) (μg Chl-*a*·h)$^{-1}$. Final values are 95% CI among replicates. AP was not measured in B3 or for Initial in B2.

	Initial	Final CTL	Final +P	Final +Si
B1	15.8	39.2–50.9	28.0–33.8	
B2	NA	33.2–52.7	46.9–63.5	
B4	9.3	33.2–66.1		59.2–79.6

For experiments where alkaline phosphatase (AP) was measured, final AP activity was significantly elevated compared to initial, ambient lake levels (Table 3). In +P treatments, AP activity was not consistently lower than Control levels, consistent with the observation that all added P had been removed by biological uptake. At the end of each experiment, AP activities were consistently higher than initial levels.

Pigments

Increases in Chl-*a* and phycocyanin (PC) occur in Barton Pond in August of each year corresponding with presence of *Microcystis* (Lehman 2007). Surface Chl-*a* and PC concentrations as well as Secchi disk transparency depth varied considerably from 2003 to 2005 (Fig. 2). Not surprisingly, AOV detected statistically significant effects of both Year ($P < 0.01$) and Month ($P < 0.05$) for the transformed variable LN(Chl).

CDOM as a predictor of DOC and DON

UV absorbance (cm^{-1}) at 254 nm (CDOM) was a good predictor of DOC concentration:

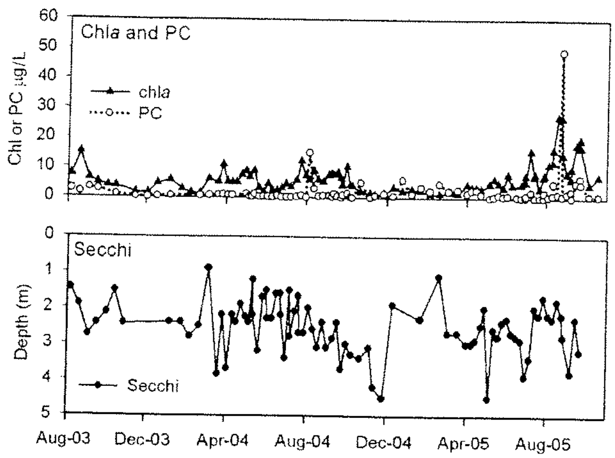

Figure 2.-Chl-*a*, phycocyanin (PC), and Secchi depth for Barton Pond from August 2003 to August 2005.

Table 4.-Medians (and ranges) of percent variance explained by year or month for state variables measured at 6 sites, from June to September 2003–2005, and for Chl-*a* measured at Barton Pond. Secchi transparency was measured at Barton Pond from 1998 to 2006. K_{25}, pH, and Secchi were not transformed; other variables were logarithmically transformed.

Variable	Year	Month
K_{25}	68.3 (54.6–72.6)	6.5 (2.5–25.3)
pH	51.6 (40.6–74.3)	6.3 (2.1–11.5)
NO_3	22.2 (16.4–24.5)	55.2 (48.6–63.3)
DN	24.3 (19.1–26.6)	56.5 (47.1–58.8)
PN	23.9 (13.2–46.1)	22.3 (1.7–44.3)
TN	24.1 (17.7–27.9)	56.7 (51.6–61.3)
CDOM	76.8 (71.0–78.6)	18.6 (14.4–20.9)
SRP	31.0 (16.9–38.6)	16.0 (7.1–27.8)
DP	27.3 (12.7–44.2)	16.4 (7.7–21.0)
TP	14.2 (4.3–16.2)	30.9 (13.7–46.8)
Chl-*a*	21.0	35.0
Secchi	23.3	20.4

$$\mu\text{M DOC} = 1658\ (\text{SE} = 146)\ \text{CDOM} + 160\ (\text{SE} = 31);\ (r^2 = 0.88,\ n = 20) \quad (5)$$

CDOM was less strongly a predictor of DON at individual sites ($r^2 = 0.33$), but the relationship was nonetheless highly significant ($P << 1.0 \times 10^{-10}$).

$$\mu\text{M DON} = 42.5\ (\text{SE} = 3.4)\ \text{CDOM} + 22.2\ (\text{SE} = 0.8);\ (n = 309) \quad (6)$$

Hydrology and nutrient concentrations

River discharge, Q, and all chemical properties except K_{25} and pH appeared lognormally distributed based on graphical inspection and ratios of mean to median far greater than 1. Statistical tests, therefore, were performed on the natural logarithms of discharge and most chemical variables.

Repeated measures of ANOVA detected strong differences among sample sites for all variables ($P << 0.00001$ in all cases). Specific conductance consistently increased downstream ($P < 0.0001$ in all sequential pairwise station contrasts), and so did pH ($P < 10^{-5}$) in all cases except HR5 and HR6, which were indistinguishable ($P = 0.98$). The 2 stations upstream of all impoundments (HR1 and HR2) were indistinguishable with respect to all nutrient variables (N species, P species, and CDOM) at $\alpha = 0.05$, but pairwise contrasts between successive stations downstream always identified significant differences in 2 or more of the 4 possible contrasts.

Temporal variation from June to September was tested by two-way AOV, using Year and Month of year as independent factors. Statistical significance of both Year and Month was established for N variables and CDOM at all sites, and for K_{25} at most sites, at the level of $P = 0.05$ or far less. For pH, there was no significant effect of Month, but interannual variation existed at all sites ($P < 0.02$). No interannual variability was detected for TP ($P > 0.05$ at all sites), but the Month effect was statistically significant. For SRP and DP, interannual variation was significant at only half of the sampling sites, whereas Month effects were common. The proportion of variance explained by Month and Year together was impressive for some variables, accounting for 0.92–0.96 of variance in CDOM; 0.71–0.81 for K_{25}; and 0.66–0.85 for NO_3, DN, and TN. For SRP, DP, and TP the temporal model was able to explain only 0.22–0.61 of the variance in the data set.

Medians and ranges of the percent variance explained by Month tended to be higher than that explained by Year for dissolved N species at our 6 river sites (Table 4). Particulate P, likewise, had a strong monthly component to its variance, and thus so did TP. For this analysis, variance associated with the year-month interaction terms was included with the Year fraction.

The hypothesis that seasonal variation was primarily the consequence of river flow, Q, was tested by linear regression of chemical concentrations (log-transformed where appropriate) against the logarithm of Q. There were little to no significant linear relationships between chemical property values and Q for K_{25}, pH, PN, SRP, DP, or TP. Nitrogen variables and CDOM did show significant linear relationships that were positive in all cases, but the proportions of variance explained by Q were lower in all cases than the amounts explained by month and year. The significant results for DN and TN were traceable to NO_3; when NO_3 concentrations were subtracted from DN and TN, the statistical significance of Q disappeared ($P > 0.2$). When the data set was adjusted for seasonality by subtracting monthly means from the raw data, only a statistically insignificant ($\alpha = 0.05$) 6% the residual variance was explained by correlation with ln(Q).

Daily river discharge, Q, was strongly autocorrelated. Values of the autocorrelation function declined linearly ($r^2 = 0.9996$) by 0.019 d^{-1} for time lags from 1 to 15 days. River chemistry data were not uniformly spaced in time, and an interpolation scheme had to be selected to estimate concentrations between sample dates. In the absence of evidence that concentrations varied more strongly with Q than with time, a simple linear interpolation of measured concentrations was chosen.

Detection power

The preceding statistical analyses caused us to aggregate water quality data as follows:

1. By month and year: K_{25}, CDOM, Chl-*a*, and all nitrogen species
2. By year: pH
3. By month: all phosphorus species and Secchi depth

We adopted the same approach as Knowlton *et al.* (1984) and Knowlton and Jones (2006) for estimating an approximate coefficient of variation ("CV") for log-transformed variables:

$$\text{"CV"} = 50\,[\exp(s) - \exp(-s)] \qquad (5)$$

where s is the standard deviation of the log-transformed variable. Median values and ranges for the resulting "CV"s are generally low for K_{25} and pH, but they range in excess of 100 for PN, NO_3, and SRP (Table 5). The following target magnitudes of change in mean values of state variables were selected for investigation: 10% change in K_{25}, 0.2 unit change in pH, and 25% change in all other properties. Sample size requirements were calculated assuming a step change in mean value of the property, and assuming variance remains unchanged. Sample sizes, n, that would be needed to detect changes of target magnitude at each sampling site, given the established reference "ordinary" variability, were calculated according to Eq. 4. These numbers were then divided by 4 to simulate the assumption that future sampling frequency would duplicate the frequency used to generate the reference data set (weekly, or about 4 samples per month). Resulting from this calculation are the putative numbers of years required to detect statistically significant changes in the different properties at specified detection limits (Table 6). Baseline variability is small enough for some properties that changes could be detected in a single year (specific conductance, pH, DN, TN, and CDOM). A 25% change in TP should be detectable within 2 years, as should be a 25% change in Secchi transparency depth. The most problematic properties are particulates (PN and Chl-*a*) as well as the inorganic nutrients nitrate and SRP. Detecting statistically significant changes in these properties could take up to a decade or more of intense sampling.

Table 5.-Medians (and ranges) of approximate "CV" for state variables measured at six sites, from June to September of 2003 to 2005, and for Chl-*a* measured at Barton Pond. Secchi transparency was measured at Barton Pond from 1998 to 2006. K_{25}, pH, and Secchi were not transformed; other variables were logarithmically transformed.

Variable	Median "CV"	Range
K_{25}	4.6	1.8–16.2
NO_3	54.0	17.3–138.4
DN	20.4	14.0–34.8
PN	86.6	24.0–231.9
TN	20.0	14.8–39.1
CDOM	14.3	6.4–35.4
SRP	57.5	32.3–144.8
DP	34.9	18.4–61.6
TP	30.5	13.2–47.2
Chl-*a*	49.7	45.1–58.5
Secchi	19.7	15.9–26.5

Table 6.-Numbers of years (medians and ranges) required to detect a 25% change in monthly mean value for specified properties at any of 6 sites, and for Chl-*a* and Secchi transparency measured at Barton Pond, under the assumption that sites are sampled 4 times per month from June to September.

Variable	Median	Range
K_{25} (10% change)	1	1–1
pH (0.2 unit change)	1	1–1
NO_3	7	1–34
DN	1	1–3
PN	17	2–67
TN	1	1–4
CDOM	1	1–3
SRP	8	3–37
DP	3	1–9
TP	2	1–6
Chl-*a*	8	6–14
Secchi	2	1–3

Table 7.-Summary statistics of flushing times (days) for 3 impoundments from June 2003 to September 2005.

	Barton	Argo	Geddes
Mean	4.4	2.2	3.5
Median	3.7	1.8	2.8
Minimum	1.4	1.1	1.3
Maximum	11.6	6.4	11.2

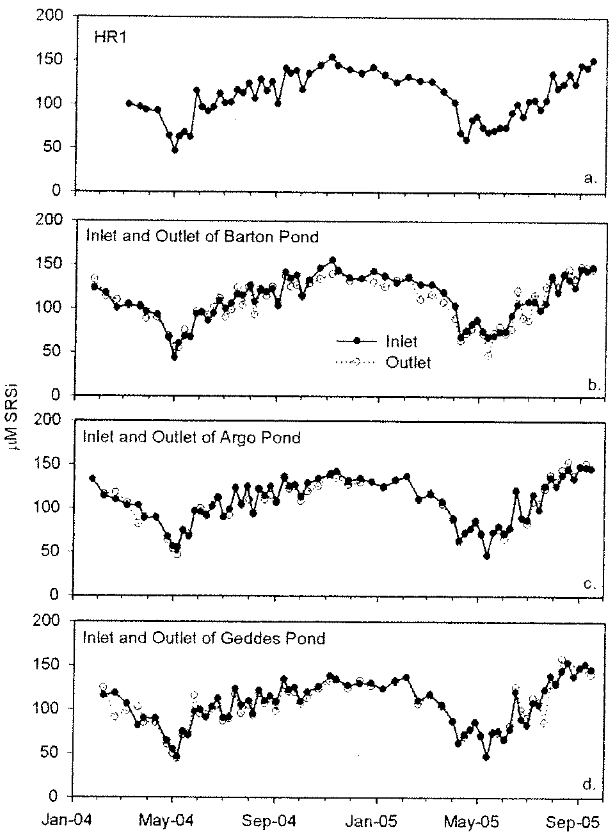

Figure 3.-Silica concentrations at the start of the study region (a), inlet and outlet of Barton Pond (b), inlet and outlet of Argo Pond (c), and inlet and outlet of Geddes Pond (d).

Table 8.-Nutrient budgets (with SE), as outflow minus income in thousands of moles, from September 2003 to August 2005.

	TP	DP	TN	DN	NO_3
Barton Pond	12 (35)	54 (18)	3,600 (2,600)	4,200 (2,500)	2,500 (4,200)
Argo Pond	−14 (33)	20 (20)	1,500 (2,700)	930 (2,500)	1,200 (4,200)
Geddes Pond	160 (37)	49 (22)	4,200 (2,900)	4,300 (2,600)	3,500 (4,500)

Retention times

Flushing times for the 3 impoundments ranged from a minimum of 1.1 days for Argo Pond to a maximum of 11.6 days for Barton Pond (Table 7).

Silica

Silica concentrations entering the study site and entering and leaving each subsequent impoundment become depressed in April and May, a time typically associated with increased diatom growth (Fig. 2). However, the depressed levels originate from circumstances upstream to our study site. Silica levels entering the study site show this characteristic silica depression, but concentrations do not exhibit appreciable additional declines between inlets and outlets of Barton, Argo, or Geddes Ponds.

N and P budgets

Net nutrient budgets (outflow minus income) for the three ponds over 2 years reveal a tendency for all ponds to act as N and P sources during the study period except for Argo Pond for TP (Table 8), but mass balances are calculated as the differences between two large numbers, each of which possess estimation errors. Most of the propagated uncertainty in the budgets traces to interpolated nutrient concentrations. We used the median approximate CVs from Table 5 divided by the square root of the number of sampling dates, n (typically n = 81 over 2 years) to estimate uncertainty, as percentage standard error of the mean, associated with fluxes either into or out of each impoundment. The square roots of the summed squares of income and outflow errors are reported as the standard errors of the net budgets in Table 8. In almost all cases, mass balance cannot be considered significantly different from zero at $\alpha = 0.05$.

Discussion

Although we used a criterion of 25% change in mean property values rather than the 2-fold step change investigated by Knowlton and Jones (2006), our results can be compared with theirs when the different frequencies of sampling are taken into account. They found that 3–8 years of monthly sampling would be needed to detect 2-fold changes in TP, TN, or Chl-*a*. We find it would generally take 1 or 2 years of sampling 4 times per month to detect 25% changes in Secchi depth, DN, TN, CDOM, and TP. The same can be said about a 10% change in specific conductance or a 0.2 unit change in pH. For SRP, NO_3, PN, and Chl-*a*, however, it could take 7–8 years, or even longer, for even weekly samples to detect a 25% change with statistical confidence. For the specific case at hand, a municipal ordinance banning lawn fertilizers with P was enacted based on the expectation that a 22% reduction in TP loading to the Huron River would result. The prediction could likely be tested with 2 years of effort.

Silica depression occurs during April and May at the entry to the study site. Little to no additional silica depletion occurs in the impoundments, and no large diatom populations were ever observed in Barton, Argo, or Geddes ponds. The flushing times of these impoundments during the spring are too rapid to permit limnetic diatom populations to develop. They fall in the very low end of the range of "transitional" lotic-lentic impoundments studied by Søballe and Kimmel (1987) to the extent that algal populations would not be expected to make full use of available nutrients (Pridmore and McBride 1984). In fact, the median retention times of Argo and Geddes Ponds are <3 days (Table 7), a critical value identified by Basu and Pick (1995) for net increases in algal standing crop. Ferris and Lehman (2007) demonstrated how variations in hydrology controlled the size of the spring diatom bloom during 2004, 2005, and 2006 in Ford Lake, a much larger man-made lake located downstream from Geddes Pond (Fig. 1). The largest vernal bloom of diatoms occurred in April 2004, when lake flushing time exceeded 20 days.

From February through April 2005, silica concentrations in Barton Pond never dropped below 69 μM. The quantity of silica available in Barton Pond seems sufficient for maximal diatom growth; adding SRSi did not result in enhanced diatom production in experiments. Phosphorus addition did result in increased Chl and PN with respect to control. Moreover, AP analyses in P addition experiments are indicative of phosphorus depletion.

These experimental findings are consistent with, and explanatory for, the inability of our mass balance calculations (Table 8) to detect either retention or export of N and P from any of these riverine impoundments. Sampling frequency was sufficient to characterize income and outflow fluxes to within 2–3% of the means in most cases. However, net differences between income and outflow were at these same levels. The flushing rates of these impoundments permit insufficient time for *in situ* communities to alter the biogeochemistry detectably. When water samples are enclosed and permitted to incubate for several days without washout, however, we demonstrated that the water chemistry could indeed be markedly altered by the resident species.

Aphanizomenon and *Microcystis* appear in Barton Pond during the late summer. Whether these algae are capable of forming nuisance blooms in Barton Pond is a matter of concern in this municipal water supply; however, the short flushing times, in part due to withdrawal of drinking water, probably work to mitigate this possibility.

A literature review conducted by Knowlton and Jones (2006) suggests that the magnitudes of variation, and resulting detection limits, we documented in this study may be universal. Studies by Larsen *et al.* (1995, 2001), Smeltzer *et al.* (1989), Terrell *et al.* (2000), and Walker (1985) generally ascribe lower levels of interannual variability to Secchi transparency (maximum CV = 22%) than to Total P (maximum CV = 40%), or Chl (median CVs of about 25%). The literature generally indicates month-to-month CVs exceed interannual variations.

For properties we can compare directly, we likewise found seasonal variation to exceed year-to-year differences for TN, TP, and Chl. However, we found seasonal and interannual variation to be of similar magnitude for Secchi depth, and that interannual differences exceeded seasonal variations for specific conductance and CDOM.

The generality of these results can be incorporated in the design of impact assessment studies. For example, ordinances banning P in fertilizer, future dam removals, or treated wastewater discharges can be considered as experimental perturbations. The sampling effort that would be needed over time to detect changes of any *a priori* prescribed magnitude can be estimated. This type of analysis provides the best information for available time and money, and thereby creates a realistic view of detection ability and Type II error.

Acknowledgments

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Stormwater
The Journal for Surface Water Quality Professionals
November 3rd, 2008 9:17am PST

River Phosphorus Drops Following P-free Fertilizer Ordinance

Posted By John T. Lehman Comments

How hard would it be to learn if river phosphorus concentrations are dropping in response to a new city ordinance restricting the sale and use of lawn fertilizers containing phosphorus? That is the question posed to me about a year ago by the environmental coordinator of the city of Ann Arbor, Michigan. Like several other communities in Michigan, as well as in New Jersey, Wisconsin, Florida, and entire states including Maine and Minnesota, the city council had voted to take a step that they thought would be good for the environment. They hoped to limit the amount of phosphate runoff from residential properties and maybe curtail eutrophication of the scenic Huron River.

It so happened that a student, Julie Ferris, and I were putting the final touches on a scientific study that we were planning to publish in Lake and Reservoir Management, the journal of the North American Lake Management Society (NALMS). As part of that work we had been examining the statistical properties of a water quality dataset that I collected for the Huron River from 2003 to 2005. I used the data to calculate nutrient loads for an EPA-sponsored research project on some downstream lakes, but we had become curious about the magnitude of the "ordinary variability" that we could expect from year to year and month to month. The data had an unusual high degree of temporal resolution, with measurements at weekly and sub-weekly scales. And we were focusing on a subset of the data that included the city of Ann Arbor and points upstream of it (Figure 1).

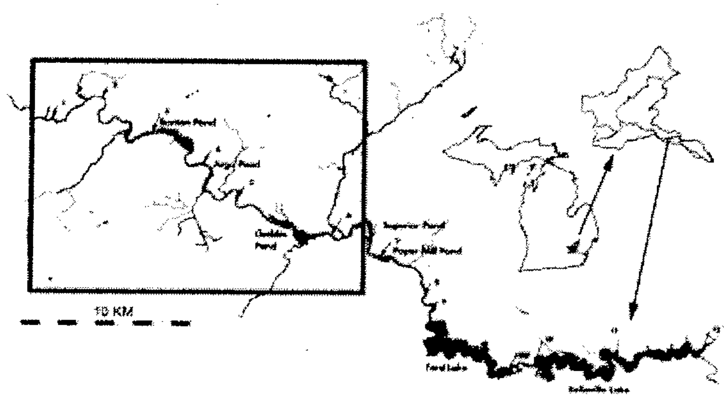

Figure 1. The Huron River of southeastern Michigan. The study region is enclosed in a rectangle.

"How big a change were you expecting to get from this ordinance?" I asked. "About 22%," was the reply. Now this was a question that actually has an answer, or many answers depending on how you construct the statistical model. The trick is in how you balance Type I and Type II error.

Recall that Type I error occurs when you mistakenly accept a hypothesis as true when it is really false. Type II error happens if you reject a valid conclusion because you think it is false. There are big sample size and effort problems with trying to minimize both types of error simultaneously. Besides, in this case the historical data were what they were, and we could not go back in time and collect more. So we set Type II error to 75% (chance of detecting a decrease if it is real) and Type I to 10% (chance of thinking the effect is real when it is not).

Three operational measures of phosphorus (P) were at issue. The first is total phosphorus (TP), the total mass of P in all forms: dissolved, colloidal, and particulate. The second is total "dissolved" phosphorus (DP), defined as the phosphorus in filtrate that has been passed in our case through a filter with 0.45 micrometer aperture size. The final is "soluble" reactive phosphorus (SRP), or the amount of P in the filtrate that can be measured by reacting it with molybdate ion in an acid solution, but without chemically digesting all the organic compounds present.

Across the various sample sites in our historical data set we discovered that SRP was more variable than DP, which in turn was more variable than TP. Our model told us that the median time it would take to detect a 25% change, collecting weekly data from May to September, was eight years for SRP, two to three years for DP, and one to two years for TP. We published the prediction (December 2008 issue of LRM).

A Test of the Prediction
While the paper waited in its publication queue, the city asked to fund a student to conduct a study under my supervision, since we were measuring nutrients all the time in the course of our lake research. I had to confess some skepticism, however. The city had reasonable control over what the lawn care businesses were applying and what was for sale in local stores, but nobody had a real clue about the extent of compliance, and that seemed a weak link. It was a chance to teach a student some useful analytical and statistical methods, though, and Doug Bell was enthusiastic about the opportunity.

We decided to approach the problem as a field experiment. Experiments need "controls." We selected two kinds of controls: a control site and control variables. The control site was the station labeled as "1" in Figure 1. It lies several miles upstream from the city limit of Ann Arbor and outside the jurisdiction of the city ordinance. Our experimental sites are labeled 5 and 6 in Figure 1. The first has about 29 square kilometers of drainage attributable to Ann Arbor, and the second has about 94 square kilometers. We call these two sites A and B, respectively. Control variables were chemical properties that had nothing to do with phosphorus. We selected nitrate, silica, and colored dissolved organic matter (CDOM), a measure of humic acids in the water.

Thus there were three control variables and three response variables (SRP, DP, and TP); one control site; and two experimental sites. The statistical test was a simple t-test contrasting the 2008 data with the reference data stratified by month. All six of the water chemistry variables had lognormal frequency distributions, so they were log-transformed before analysis. The months tested were May to September.

Control Variables
There were no statistically significant differences in silica concentrations at any site for any month. CDOM was higher in 2008 than the reference period at both experimental sites only in the month of July. Otherwise, there were no differences. Nitrate was significantly different for two months each at all three of the sampling sites, one time higher, and one time lower. In short, the control variables had basically the same values in 2008 that they had from 2003 to 2005.

Phosphorus Variables
SRP behaved much like the control variables. There was no statistical evidence of altered concentrations at any site in any month. But given the variability of the reference data, we had predicted it would take eight years to see an effect of 25% magnitude. The prospects were better for DP and especially TP. Figures 2 and 3 show the findings for these response variables. First of all, there are no significant decreases in DP or TP at the control site for any month. For TP, however, there were statistically significant decreases at site B in four months out of the five, and there was a trend of decreasing concentrations at both sites for every month but September for A. DP also exhibited a trend of decreasing concentrations at site B every month, but the differences exceeded the level of statistical significance for only one month at each site.

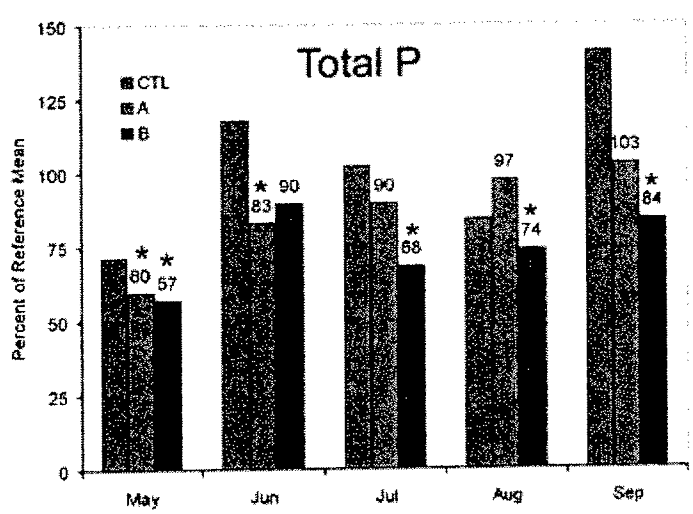

Figure 2. Average concentrations of TP measured in 2008 expressed as percent of 2003-2005 values. * signifies that the reduction is statistically significant.

Site B, you recall, receives runoff from three times the city drainage area as site A. The odds of the DP levels at site B being less than the reference period for five months in a row are the same as those for flipping a coin and getting five heads in a row.

These results seemed worth sharing with professionals who may be contemplating the possible value of an ordinance like Ann Arbor's, coupled with environmental education efforts, in their own communities. For the six statistically significant TP reductions flagged by asterisks in Figure 2, the average decrease was 31%.

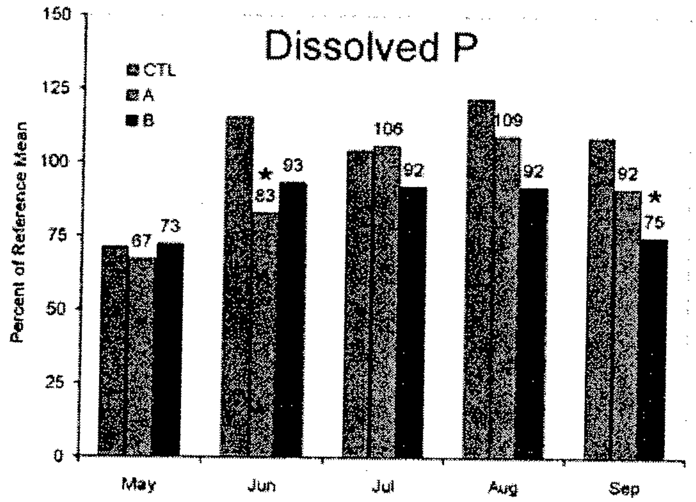

Figure 3. The same as Figure 2, but showing results for DP.

It is possible to state objectively with a considerable degree of confidence that phosphorus concentrations were lower in 2008 at experimental sites compared with the reference period (2003 to 2005) and that the reductions were coincident with a city ordinance restricting use of lawn fertilizers containing phosphorus. It would be tempting to conclude that the phosphorus reductions were caused by implementation of the ordinance, and that may indeed be the case. However, we must bear in mind that the ordinance was enacted in the context of public education efforts that encourage citizens to be more mindful of yard waste discharges into storm drains, to exert more diligence regarding buffer strips of vegetation along stream banks, and to exhibit more environmental awareness in general. These multifaceted efforts make it difficult to isolate a single cause for the changes, but the changes appear to be real.

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Reduced river phosphorus following implementation of a lawn fertilizer ordinance

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Abstract

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Statistical comparisons of 2008 surface water quality data with a historical data set at weekly and subweekly resolution revealed statistically significant reductions in total phosphorus (TP) and a trend of reduction in dissolved phosphorus following implementation of a municipal ordinance limiting the application of lawn fertilizers containing phosphorus. No reductions were seen at an upstream control river site not affected by the ordinance. Nontarget analytes including nitrate, silica and colored dissolved organic matter did not change systematically as did P. The data were analyzed in the context of a statistical model that characterized historical temporal variability and predicted the sampling effort needed to detect changes of specified magnitude. Expected changes of about 25% in monthly mean value were predicted to require weekly samples during the summer for only 1 or 2 years for TP; statistically significant reductions measured after 1 year averaged 28%, or about 5 kg P/day. The lawn fertilizer ordinance was only one component of broader efforts to reduce nonpoint source loading of P, however, so the magnitude of its role in the measured changes remains uncertain.

Key words: eutrophication, sampling requirements, temporal variation, watershed

Growing numbers of municipalities and state governments have adopted or are considering the adoption of restrictions on residential use of phosphorus-containing fertilizers. The actions are based on awareness that phosphorus (P) is often not a growth-limiting nutrient in many terrestrial soils, and that excessive application of the element leads to runoff and eutrophication of surface waters (e.g., Carpenter *et al.* 1998). Examples include the state of New Jersey, with over 100 municipalities affected (New Jersey 2007); Sarasota County, Florida (Sierra Club 2007); the state of Maine (Maine 2008); and Dane County in Wisconsin (Dane County 2007).

Aside from the environmental consciousness of the actions, little evidence exists that the bans are having a salutary effect. For example, the state of Minnesota enacted a law to regulate the use of phosphorus lawn fertilizer with the intent of reducing unnecessary phosphorus fertilizer use. The law, which went into effect in 2004 in the Twin Cities metropolitan area and statewide in 2005, prohibits use of phosphorus lawn fertilizer except in prescribed instances. However, field studies to examine the efficacy of the ban for improving surface water quality were inconclusive (MDA 2007), a fact attributed to excessive variability in runoff data. The problem may indeed be the statistical power of available datasets. Vlach *et al.* (2008) analyzed more than 500 data points and reported reductions in P runoff from sub-watersheds in Minnesota, where the use of fertilizer containing P was restricted in 1999, compared to other sub-watersheds where the ban was not imposed until 2004. The study involved pair-wise comparisons of 6 subwatersheds in the municipalities of Plymouth and Maple Grove, Minnesota. The sites differed in their regimens of fertilizer use, with the Plymouth sites using only P-free fertilizer, and Maple Grove sites serving as controls using P-containing fertilizer. Concentrations of total P in runoff were virtually identical between the 2 treatments, but soluble reactive P concentrations in runoff were 17% lower at the P-free sites.

As part of its efforts to comply with a state-imposed phosphorus total maximum daily load (TMDL) that called for a 50% reduction in P discharges to the Huron River, the city of Ann Arbor in southeast Michigan enacted an ordinance

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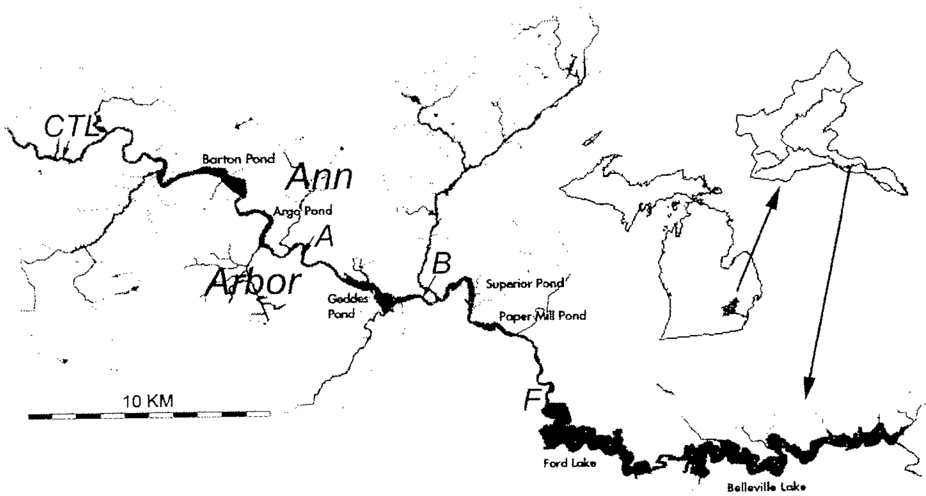

Figure 1.-- Study site, with sampling stations identified.

that went into effect in 2007 (Ann Arbor 2006) to limit phosphorus application to lawns. Compliance with the lawn fertilizer ordinance depends on restriction of phosphorus fertilizer application by homeowners and lawn care services unless they have a soil test demonstrating need. The estimated effect of full compliance was a 22% reduction in P entering the river. The prediction was obtained by estimating the lawn fertilizer runoff from a creekshed within the city and extrapolating that result to all other creeksheds. Ferris and Lehman (2008) used their historical set of Huron River water quality data to predict the sampling effort that could detect changes of roughly 25%. They concluded that a 25% reduction in total P (TP) would be detectable after 1 or 2 years of sampling 4 times per month. Similar percentage reductions in dissolved P (DP) would likely take 2 or 3 years, and for soluble reactive P (SRP), the time could be as long as 8 years. This paper reports the test of the *a priori* predictions after 1 year.

Study site

Our field site (Fig. 1) was a portion of the Huron River catchment in southeastern Michigan (United States Geological Survey, USGS Cataloging Unit 04090005). Four stations were established (Table 1) on the basis of an existing historical data set at weekly and subweekly intervals (Ferris and Lehman 2008). The station designated Control (CTL) corresponded to station 1 of Ferris and Lehman (2008). It was upstream from Ann Arbor and outside the jurisdiction affected by the city ordinance. Stations A and B corresponded with Ferris and Lehman's stations 5 and 6. Station A represents about 29 km^2 of catchment attributable to Ann Arbor, and station B represents about 94 km^2. A fourth station, F, was downstream at the site where the Huron River discharges into Ford Lake, a eutrophic impoundment. Station F was downstream from the outfall of the wastewater treatment facility that serves Ann Arbor (AAWWTP); stations A and B were upstream of the outfall. Water quality data at station F have been reported by Ferris and Lehman (2007), and include 4 years (2003–2006) prior to implementation of Ann Arbor's fertilizer ordinance.

Field sampling

Water was collected at weekly intervals from May to September 2008. Raw water was filtered on site for nutrient analysis using Millipore™ disposable filter capsules of nominal 0.45 μm pore size.

Nutrient analyses

Analyses included SRP, DP, TP, soluble reactive Si (SRSi), pH, and nitrate (NO_3). The SRP was measured as molybdate-reactive phosphate in filtrate; DP and TP were measured as

Table 1.-Locations and approximate catchment areas of 4 Huron River stations that are attributable to Ann Arbor. Coordinates are specified as eastings and northings for UTM Zone 17.

Station	E	N	Catchment area attributable to Ann Arbor (km^2)
CTL	262796	4691655	0
A	275285	4685262	29
B	279744	4683268	94
F	284834	4679126	94 + AAWWTP outfall

SRP after first oxidizing filtrate (DP) or unfiltered water (TP) with potassium persulfate at 105 C for 1 h. Specific conductance at 25 C (K_{25}, μS) was measured with samples at 25 C in a water bath. Colored dissolved organic matter (CDOM) was measured as UV absorbance at 254 nm. Ferris and Lehman (2008) showed that CDOM correlates strongly with both dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in the Huron River. All nutrient analyses were performed according to Ferris and Lehman (2007). For SRP and TP, 3 replicates were measured at each site. For DP, 2 replicates were measured at CTL and station A, and 3 replicates were measured at stations B and F. Sample means and standard error of the mean (SE) were calculated for each determination and additional replicates were added if the ratio of SE to mean exceeded 0.05.

Daily volumetric discharge and mean daily TP concentrations in the effluent of the AAWWTP were supplied by the city of Ann Arbor from the operator's logs.

Statistical methods

The primary response variables of interest were SRP, DP and TP; however, NO_3, CDOM, SRSi, pH and K_{25} were included as nontarget or quasicontrol variables because we reasoned that they should be unaffected by a nutrient reduction strategy specifically targeted at P. We adopted the statistical model developed by Ferris and Lehman (2008) with the aim of testing the efficacy of the new ordinance; it balanced type I error against type II error such that $\alpha = 0.1$ and $\beta = 0.75$. The object was to hold type I error reasonably low while seeking a credible level of power to detect environmental changes if they indeed occur. Because we wished to test the model predictions, we set $\alpha = 0.1$ for significance testing. Our *a priori* expectation was that P concentrations would decrease, and so we applied one-tailed tests to the P data. Because we had no *a priori* expectations regarding the nontarget variables, we applied two-tailed tests and set $\alpha = 0.1$ to mimic the threshold probability applied to P variables.

We log-transformed SRP, DP, TP, NO_3, SRSi and CDOM prior to statistical comparison and used K_{25} and pH in statistical tests without transformation. Based on previous work we expected that values from the different sampling stations would differ and that there would be significant differences in mean monthly concentrations. To partition variability contributed by these factors while testing differences between the control and treatment sites and between the pre-ordinance and post-ordinance years, a MANOVA (SAS) was used to assess overall changes in concentrations of the three P variables simultaneously, using station, month and year (reference period vs. 2008) as categorical factors. All 3 factors proved statistically significant ($P < 0.02$ for both SRP and DP; $P < 0.0001$ for TP). We subsequently explored the data with attention to detailed response by station, particularly control versus experimental as well as the direction of change.

All original data used in these analyses are archived for public access at http://www.umich.edu/~hrstudy/dataarchive.htm.

Hydrology

Fluvial discharge of the Huron River at Ann Arbor (USGS 04174500) during 2008 was qualitatively similar to discharges recorded during the reference years, with the exceptions of unusually high discharges during late May 2004 and late Sep 2008 (Fig. 2).

Nontarget variables

Analysis of variance (AOV, SYSTAT version 10) revealed that SRSi concentrations varied significantly by month ($P < 0.0001$) but not by station or year ($P > 0.19$). Nitrate varied significantly by station and month ($P < 0.0001$) but not by year ($P = 0.49$). In comparison, CDOM varied by month ($P < 0.0001$) and by year ($P = 0.007$) but not by station ($P > 0.6$). Across all stations, including CTL, CDOM was on average about 8% higher in 2008 compared with the reference period, suggesting that DON or DOC levels were elevated. Specific conductance was similarly on average about 9% higher in 2008 than the reference period across all stations including CTL ($P < 0.0001$), and pH was significantly higher by about 0.1 unit ($P < 0.0001$). Temporal patterns in CDOM, specific conductance and pH seemed to correspond with the seasonal pattern of river flow variation in 2008. As flow slackened in July and August, these properties increased at all stations, including CTL.

Phosphorus variables

As anticipated from past sampling experience, SRP was more variable than DP or TP (Fig. 3) and there was no indication that concentrations for the months of May to September in 2008 were significantly lower than reference values at any site other than station F in August. For DP, a trend of decreasing mean concentrations was observed at the experimental stations, particularly B and F (Fig. 3); however, TP concentrations were repeatedly lower than reference at the 90% probability level, particularly at stations B and F (Fig. 3).

The magnitude of the concentration decreases observed at station F downstream of the AAWWTP outfall were indistinguishable from the decreases observed at upstream station B. Paired t-tests of the concentration differences by month

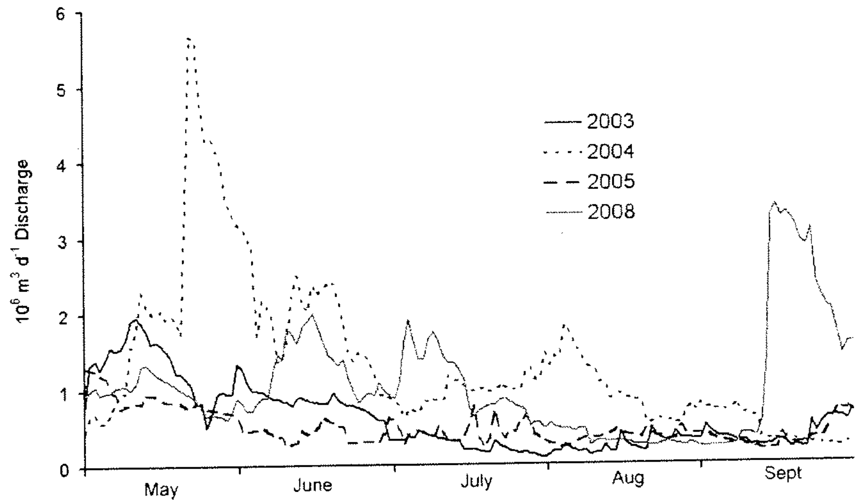

Figure 2.-Fluvial discharge of the Huron River at Ann Arbor (USGS 04174500) from May to September for 3 reference years (2003–2005) and the post-ordinance test year 2008.

for 2008 compared to the reference period differed neither for TP ($P = 0.83$) nor for DP ($P = 0.13$). Analysis of TP discharge records for the AAWWTP (Fig. 4) revealed that 2008 discharge levels were within the range observed during the previous 5 years.

Discussion

Ferris and Lehman's (2008) median estimate of the effort needed to detect a 25% change was 8 years of weekly samples for SRP but only 2 years for TP and 3 years for DP. The results of this study after 1 year are consistent with those predictions. A reduction in SRP was detected at only one site on one date, whereas reductions were detected for both DP and TP at experimental sites with greater regularity. A summary of key findings follows:

- Decreases in TP concentration at 90% confidence were noted in 10 cases out of 15 at the experimental sites (A, B and F) during the main growing period from May to September (Fig. 3). Moreover, a trend of reduced (mean) TP concentrations was observed at the experimental sites in 14 cases out of 15. Reductions at station B, just upstream from the AAWWTP outfall, were more regular than at station A. Station B receives considerably more cumulative drainage from Ann Arbor than does station A and may therefore be more responsive. The average reduction in concentration for the 10 statistically significant cases was 28%.
- Reductions in concentration of DP were rarely significant at 90% confidence level at the experimental sites (Fig. 3), although a trend of reduced monthly mean concentrations was observed at the experimental stations, with the mean reduction being 13% overall.
- The magnitudes of the DP and TP reductions at station F, downstream from the AAWWTP outfall, were indistinguishable from DP and TP reductions measured at station B, upstream of the outfall. Combined with absence of any systematic trend in point source discharge of TP (Fig. 4), this suggests that the detectable effect traces to nonpoint source loading.
- The upstream site CTL appeared to function well as a control site, in that no reductions in SRP, DP or TP were noted.
- The nontarget variables showed no evidence of the station-specific response seen in TP and to a lesser degree in DP. Departures of specific conductance, pH and CDOM from historical conditions appeared to originate upstream of the experimental unit because they were in evidence at the control site. Consistent changes in nutrient concentrations only within the experimental unit were confined to P.
- Based on the median daily TP load carried by the Huron River at station B during May to September 2003–2005 (data from Ferris and Lehman 2008), the magnitude of the load reduction is about 5 kg P/day.

After the first year of data collection and analysis, detectable reductions have been documented for TP and, to some degree, for DP for every month from May to September. Percentage reductions are of the magnitude predicted to be detectable at the applied level of sampling effort. We can state objectively within the context of our statistical model that P concentrations were lower in 2008 compared with the

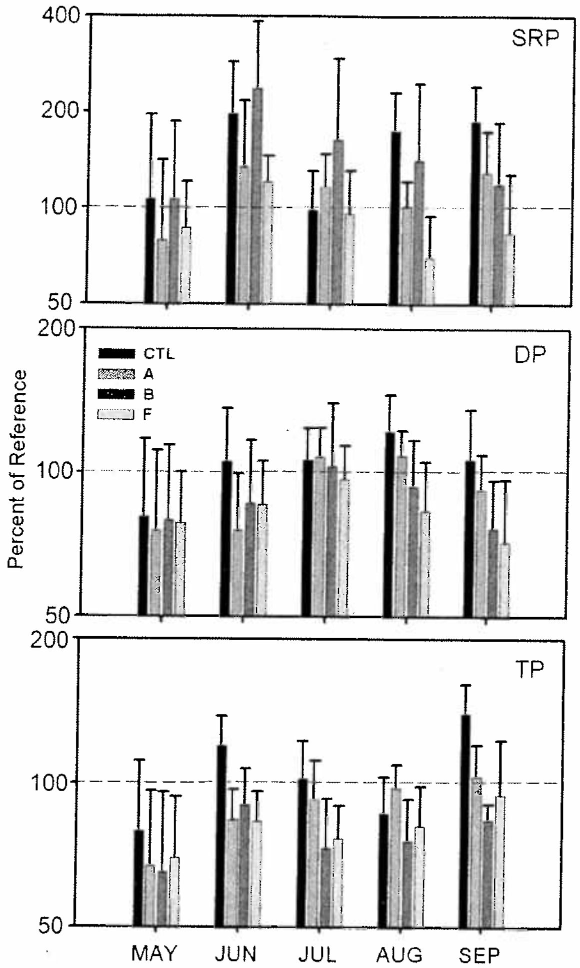

Figure 3.-Concentration anomalies of SRP, DP and TP at control and experimental sites in 2008 expressed as percent of reference values. Error bars represent upper 90% confidence intervals of the means.

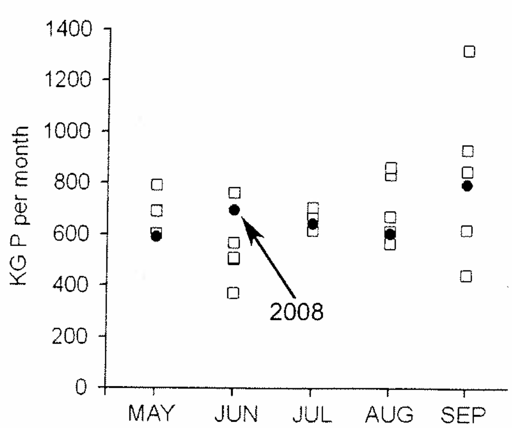

Figure 4.-Monthly discharge of TP from the Ann Arbor wastewater treatment facility from 2003 to 2008.

reference period (2003–2005) at experimental sites upstream from the AAWWTP outfall and therefore independent from treatment or discharge practices. These reductions were coincident with a city ordinance restricting use of lawn fertilizers containing phosphorus. In fact, the magnitudes of DP and TP reductions downstream of the outfall are not statistically different from those measured upstream, meaning that the 2 are highly correlated and traceable to nonpoint source loading.

The magnitudes of the TP reductions are generally greater than DP reductions, even though DP accounted for 56% (SE = 3%) of TP at all sites during the reference period and 60% (SE = 3%) of TP in 2008. This suggests that the main effect has been reduction in the particulate P load of the river. We have not tried to determine the relative contributions of biogenic or mineral particles to the total, or whether phosphate in particulate matter is biologically absorbed or physically adsorbed.

It would be tempting to conclude that the phosphorus reductions were caused by implementation of the ordinance, and that may be the case; however, the ordinance was enacted in the context of public education efforts that encourage citizens to be more mindful of yard waste discharges into storm drains, to exert more diligence regarding buffer strips of vegetation along stream banks and to exhibit more environmental awareness in general. These multi-faceted efforts make it difficult to isolate a single cause for the changes, but the changes appear to be real and of the predicted magnitude and direction. Continued measurements are certainly in order in this watershed as well as others, but the initial results suggest that with good baseline data even relatively modest (25%) changes in nutrient load can be detected against background variation on time scales fast enough to help inform policy decisions.

Acknowledgments

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Researcher: John Lehman
Date: 8/17/09

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